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An Experimental Investigation of
 Radiation Effects in Semiconductors

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INTRODUCTION

Many of the properties of semiconductors are extremely sensitive to the concentration and type of point imperfections that are present. These defects include intentional impurities such as donors or acceptors, accidental impurities such as oxygen, or intrinsic lattice defects such as vacancies and interstitials. Irradiation with high energy particles generates lattice defects-vacancies and interstitials-that may then interact with other defects and produce still other defects of a more complex type. The microscopic nature of many of these defects is unknown and the influence of these defects upon the properties of the material is poorly understood. The experiments described below are intended to provide information about the nature of the defects and about the location of the electronic energy levels that are produced by these defects. These studies are currently dealing with the effects of irradiation upon the minority carrier lifetimes of silicon, the influence of irradiation upon the recombination luminescence of silicon and germanium, and the influence of irradiation upon the conduction process at low temperature when the impurity concentration is sufficiently high that impurity band conduction predominates.

CURRENT RESEARCH

Models of several of the prominent defects that are generated in silicon by irradiation at room temperature with fast electrons have been established by electron spin resonance studies.^{1/} Of these defects, three are of particular interest to us. They have been called the Si-A, Si-E and the Si-J centers. The silicon A center consists of a substitutional oxygen atom.

The electron spin resonance is seen only when the Fermi level is closer than 0.16 eV to the conduction band. Electrical conductivity measurements have indicated that the defect is a donor with an energy level 0.16 to 0.17 eV below the conduction band. The silicon E center consists of a silicon vacancy trapped next to a substitutional phosphorous impurity. The electron spin resonance is only found when the Fermi level is closer than about 0.4 eV to the conduction band. Electrical conductivity measurements on phosphorous doped silicon irradiated with Co^{60} gamma rays indicates that this defect introduces an acceptor state 0.47 eV below the conduction band.^{2/} In p-type silicon the prominent defect appears to be a divacancy, called the Si-J center. Two states of this defect are found depending upon whether the Fermi level is nearer than 0.3 eV to the valence band or nearer than 0.47 eV to the conduction band. Since all the defects described above result from an association of a lattice vacancy with an interstitial oxygen atom, with a donor or with another vacancy, it is reasonable to expect that the relative concentration of each of the complex defects will depend upon the relative concentration of the impurities and of vacancies.

MINORITY CARRIER LIFETIME. The lifetime of minority carriers that are released in the crystal by a short pulse of light depend upon the concentration of recombination centers. Each of the defects mentioned above can, under appropriate conditions, act as recombination centers. Hall and Shockley and Read,^{3/} have shown that for a single recombination center with a small concentration of excess carriers that the minority carrier lifetime τ is given by

In order to determine the influence of dopant and oxygen content upon the minority carrier lifetime, a series of n and p-type samples of various resistivities was measured prior to irradiation. Oxygen content was varied by using zone-refined and Czochralski grown crystals. Crystals grown by the latter technique normally contain 10^2 to 10^3 more oxygen than do the former. Irradiations with Co^{60} gamma rays are underway and further measurements of τ are being made. These results are summarized in Tables I and II. Previous data taken at higher radiation doses are not reported in these tables.^{4/} The present data represent the initial stages of a systematic study of irradiation and thermal annealing. $T_{1/2}$ is the time required for one-half of the excess carriers to decay. No value of the activation energy E_R is listed unless a single unique value was observed. The following observations can be made from these preliminary data:

- 1) Float-zone grown silicon is more sensitive to irradiation than is Czochralski grown silicon.
- 2) Heat treatment prior to irradiation can significantly alter the minority carrier lifetime. A comparison of samples L_1 and L_2 suggests that the change in $1/T_{1/2}$ introduced by irradiation is not affected by the anneal.
- 3) With the exception of sample E_4 , a general correlation exists between minority carrier lifetime and room temperature resistivity for the float-zone grown material. No such correlation exists for Czochralski grown material.

Further gamma ray irradiations are underway on these samples. Hall coefficient and resistivity measurements have been made on specimens cut

from the same slice as the lifetime samples. Complete temperature measurements have been made in several cases and will be repeated following irradiations that measureably alter the lifetime.

RECOMBINATION LUMINESCENCE. Study of the recombination luminescence in silicon has been unexpectedly difficult. After many unsuccessful attempts to find this luminescence in unirradiated silicon, it became rather obvious that the surface treatment was not sufficient to produce a long surface lifetime. Since the optical excitation of the luminescence is confined to short wavelengths, for which absorption coefficients are high, it is imperative that the excess carriers have a sufficient lifetime to enable them to diffuse away from the surface in order to recombine in the bulk sample. Impurities on the surface, the nature of the oxide layer, the extent of the damaged layer resulting from cutting and polishing, and many other factors can result in non-radiative recombination of excess carriers. This problem has been solved by utilizing a treatment of the samples that closely parallels that used by Haynes.^{5/} The recombination luminescence of a sample of one ohm-cm p-type silicon is shown in the attached figure. The half width at the low temperature is not as narrow as that reported by Haynes for 77°K. Since this is a sensitive function of temperature, it simply means that better contact must be made between the sample and the coolant, in order to conduct away the large amount of heat generated by the excitation light. This presents no difficulty.

A cooled PbSe detector has been purchased from Infra-Red Industries. Calibration of this, using a radiation thermocouple as a reference, indicates that this detector is sensitive to 7.4 microns and that its response per

absorbed photon is constant to $\pm 10\%$ between 1 and 6 microns. Although this detector is inherently less sensitive than PbS, it has a much greater range of spectral sensitivity. The response of the PbS detector shows a more or less gradual decline from 1 micron to 3.4 micron, at which point its sensitivity is so low as to be of little value. These two detectors will now be used to scan the entire spectral region of interest of both silicon and germanium before and after irradiation. It now appears that all major difficulties have been resolved and that measurements on irradiated material can progress rapidly.

STUDIES OF IMPURITY BAND CONDUCTION. Changes in the impurity band conduction process as affected by irradiation will not be described in detail here since a manuscript is in the process of being completed. A summary of the work is as follows: Samples having a donor concentration between 6.7×10^{15} and $1.7 \times 10^{17} \text{ cm}^{-3}$ have been studied. Resistance and Hall coefficient measurements have been made between room temperature and 1.8°K . These samples have a normal compensation of about 4% when received. Irradiation with fast neutrons introduces deep lying acceptors which compensate a portion of the donors. The compensation has been increased to about 85% in most samples. The compensation was determined from changes in the room temperature Hall coefficient. The changes in conduction near the liquid helium yields information that is useful in examining the various models of impurity conduction that have been proposed.) For the lower donor concentrations, the model that an electron hops from an occupied donor to a neighboring ionized donor, has been well established experimentally and theoretically.^{6,7/} Data obtained in this study are in agreement with this model. At the highest donor concentrations a band is formed from the

ground states of the impurities and conduction takes place without an activation energy. As the compensation of such a sample is increased, the conduction decreases, exhibits an activation energy, and assumes the form of the conduction of a less doped sample. The mechanism of conduction in this intermediate region is less well understood. It is believed to arise from a process that involves the exchange interaction of the donor atom electrons in excited states. The results of these studies support this view. A portion of this work will be presented at the American Physical Society meeting in Kansas City in March. The abstract of this paper is attached to this report.

Measurements of the changes in the impurity conduction resulting from gamma ray irradiation have been undertaken in order to compare with results obtained on neutron irradiated samples.

Preliminary data on the thermal annealing of defects produced by the neutron irradiation of these highly doped samples indicates that the majority of the annealing occurs at temperatures above 250°C. There is virtually none of the 150°C annealing behavior present which has been observed in higher resistivity material.^{8/} These data will be extended in an effort to establish the activation energy for annealing and correlate this with the disappearance of a specific defect.

PERSONNEL

Dr. E.A. Davis left the University in November to take a position at the Xerox Corporation in Rochester, New York. Dr. E.L. Wolf completed his Ph.D. degree at Cornell University in August and began work on the impurity conduction problem in September.

Mr. Robert Spry and Mr. Ralph Hewes are continuing work on the recombination luminescence and the minority carrier lifetimes for their Ph.D. theses.

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4. See NASA TND-2364, An Experiment Investigation of Radiation Effects in Semiconductors by W. Dale Compton.
5. Dr. J.R. Haynes kindly provided us with a detailed description of his technique.
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Table I

Effect of Co^{60} Irradiation Upon Czochralski Grown Silicon

Sample	ρ (ohm-cm) (Room Temperature)	Prior to Irradiation		After $1.4 \times 10^6 R$ Irradiation	
		$T_{1/2}$ (μsec)	E_R (eV)	$T_{1/2}$ (μsec)	E_R (eV)
Q_1	p-112	38	--	unchanged	
R_1	p-250	80	--	unchanged	
I_3	n-220	365	.09	110	.10
O_1	p-20	240	--		
P_1	p-45	70	--		

Table II

Effect of Co^{60} Irradiation Upon Float-Zone Grown Silicon

Sample	ρ (ohm-cm) (Room Temperature)	Prior to Irradiation		After 2.27×10^5 R Irradiation	
		$T_{1/2}$ (μsec)	E_R (eV)	$T_{1/2}$ (μsec)	E_R (eV)
B_1	n-20	28	.07	5.8	.085
C_4	n-200	250	.134	16.5	.50
F_3	p-200	140	.085	110	.054
L_2	n-67	63	.28	7.2	.46
L_1	n-67	68	-		
L_1^+	n-65	5.6	.18	3.5	-
M_1	p-65	107	.12	75	.105
M_2	p-65	82	.145		
M_2^+	p-65	1.96	.065	2.12	.036
E_4	p-24	250	.06		

Note:

L_1^+ and M_2^+ were sample L_1 and M_2 respectively following an anneal in air at 500°C .

Abstract of paper to be presented at Kansas City meeting in March, 1965

Compensation Dependence of Impurity Conduction in Germanium^{*}, E.A. Davis[†]
(introduced by W.D. Compton), University of Illinois--The effect of compensation on the resistivity and Hall effect associated with impurity conduction processes in antimony doped germanium has been studied as a function of temperature down to 1.5°K. The compensation was varied in a controlled manner by irradiating with fast neutrons, the resulting interstitial-vacancy type damage producing the required acceptor levels. For donor concentrations less than $5 \times 10^{15} \text{ cm}^{-3}$ existing theories of impurity conduction by tunneling correctly predict the activation energy ϵ_3 associated with the temperature dependence of the resistivity. With higher donor concentrations, the resistivity and Hall coefficient exhibit more complicated behavior associated with another conduction mechanism characterized by an energy ϵ_2 . The compensation dependence of ϵ_2 is discussed with reference to proposed models for this conduction process.

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